

(19) Japan Patent Office (JP)

(12) Publication of Patent Application (A)

(11) Patent Application Laid-Open No.: Sho60-28278

(51) Int. Cl. ⁴	Identification Number	JPO File Number
H 01 L 31/10		6666-5F

(43) Publication Date: February 13, 1985

Number of Invention: 1

Request for Examination: Not filed

(8 pages in total)

(54) Photoelectric Conversion Element

(21) Patent Application No.: Sho58-138224

(22) Patent Application Date: July 26, 1983

(72) Inventor: Makoto Tsunoda

c/o Mitsubishi Electric Corporation, Material Research Institute
8-1-1, Tsukaguchi-honmachi, Amagasaki-shi

(72) Inventor: Yuji Hizuka

c/o Mitsubishi Electric Corporation, Material Research Institute
8-1-1, Tsukaguchi-honmachi, Amagasaki-shi

(72) Inventor: Shohei Eto

c/o Mitsubishi Electric Corporation, Material Research Institute
8-1-1, Tsukaguchi-honmachi, Amagasaki-shi

(71) Applicant: Mitsubishi Electric Corporation

2-2-3, Marunouchi, Chiyoda-ku, Tokyo

(74) Agent: Patent Attorney, Masuo Oiwa and two others

Specification

1. Title of the Invention

Photoelectric Conversion Element

2. Scope of Claims

(1) A photoelectric conversion characterized by having a first conductive material and a second conductive material, at least one of which can transmit light, a π -conjugated high polymer layer and an organic coloring matter layer which are interposed between the first conductive material and the second conductive material,.

(2) The photoelectric conversion element as described in claim 1, is characterized in that the π -conjugated high polymer layer is formed using at least one of polyacetylene, polyphenylenes, polyphenylene sulfide, a copolymer of polyphenylene oxide pyrrole and N-substituted pyrrole, a homopolymer of pyrrole, a homopolymer of N-substituted pyrrole, polythienylene, polyaniline, polyfuran and polyazulene.

(3) The photoelectric conversion element as described in claim 1 or 2, in which the organic coloring matter layer is formed using a compound that has a capability to sensitize the π -conjugated high polymer layer.

3. Detailed Description of the Invention

The present invention relates to a novel photoelectric conversion element.

Conventionally, as a photoelectric conversion element, a so-called solar battery has been mainly developed and put into practical use, which is obtained by forming a P-n junction in the vicinity of a surface of a silicon semiconductor. However, in addition to this, a photoelectric conversion element using a low-priced organic material is examined. Specifically, the one using a conductive high polymer material such as polyacetylene as a semiconductor, or the one using a photosensitization capability of an organic coloring matter such as phthalocyanine is examined.

A sandwich-type photoelectric conversion element using such an organic material generally has a structure as shown in FIG. 1.

The principle of operation thereof is as follows: when light (8) which has passed through a transparent or semi-transparent electrode (1) enters an organic compound layer (2), potential difference is generated at an interface between the transparent or semi-transparent electrode (1) and the organic compound layer (2) so that photo-induced electric power is generated between lead wires (5) and (7). In this case, it is necessary that an anisotropic junction (for example, a P-n junction) or a schottky

junction is formed between the transparent or semi-transparent electrode (1) and the organic compound layer (2), and further, an isotropic junction such as an ohmic contact is formed between the organic compound layer and an electrode (3). More in detail, it is necessary that the value of the work function (Fermi level) under irradiation is transparent or semi-transparent electrode $>$ organic compound layer \approx electrode, or transparent or semi-transparent electrode $<$ organic compound layer \approx electrode. As for electric power between the lead wires (5) and (7), (5) is usually an anode in the former case and (7) is an anode in the latter case. Such a principle of operation is applied to an organic photoelectric conversion element.

However, any photoelectric conversion element using an organic material as described above has disadvantages; namely, photoelectric conversion efficiency is low, photoelectromotive force that is obtained is unstable, and a lifetime is short. Therefore, there remain a lot of problems to be solved for practical application.

The present invention is made in order to overcome the disadvantages of the conventional one. It is an object of the present invention to provide a low-priced and long-lived photoelectric conversion element in which a response wavelength region is broadened and photoelectric conversion efficiency is high by providing a first and a second conductive materials at least one of which can transmit light, a π -conjugated high polymer layer and an organic coloring matter layer which are interposed between the first and the second conductive materials.

FIG. 2 is a cross-sectional view of a photoelectric conversion element according to one embodiment of the present invention. Reference numerals (9) and (12) denote conductive materials. The photoelectric conversion element can be obtained also by providing a conductive material layer over a substrate; however, the case of using a conductive material alone is shown in the figure for simplification. At least the conductive material (12) on the side that is irradiated with light can transmit light. A π -conjugated high polymer layer (10) is provided on the conductive material (9), an organic coloring matter layer (11) is provided thereon, and further, the conductive material (12) is deposited thereon to form the photoelectric conversion element. Then, lead wires (14) and (16) are connected to the conductive materials (9)

and (12) to take out electric power. It is to be noted that reference numerals (13) and (15) denote lead jointing terminals.

The photoelectric conversion element according to one embodiment of the present invention is formed as described above. Details of the principle of operation of the photoelectric conversion element is not clear at this moment; however, the present inventors and others think out any one of the following photoelectric conversion mechanisms or a mechanism in which more than two of the mechanisms are combined. That is to say:

- (I) a mechanism can be assumed, in which a P-n hetero junction is formed between a π -conjugated high polymer and an organic coloring matter when the π -conjugated high polymer is a P-type material and the organic coloring matter is n-type, and carriers (electrons and holes) generated in a junction area are charge-separated by an electric field in the junction area under irradiation so that electromotive force (or current) is induced to outside. Here, the same result can be obtained also when the π -conjugated high polymer is n-type and the organic coloring matter is P-type.
- (II) It is believed that a schottky junction can be formed between a P-type π -conjugated high polymer and a metal that has the lower work function when the π -conjugated high polymer is a P-type or a n-type material. The schottky junction is expected to be formed between the n-type π -conjugated high polymer and a metal that has the higher work function. Although a schottky junction element itself can be used as a photoelectric conversion element, an MIS element (M: metal, I: inductor, S: semiconductor) is thought out in order to increase photoelectric conversion capability. It is known that open circuit voltage is increased in this element as compared with a simple schottky element.

An organic coloring matter is considered to be used as an inductor in this MIS element.

Also, the organic coloring matter is considered to be not a simple inductor but the organic coloring matter absorbs light of a wavelength that cannot be used in

a semiconductor portion to generate carriers; the carriers are injected into a semiconductor; and electric charges are injected into a metal in order to increase conversion efficiency. In this case, a thick film (layer film) of the organic coloring matter that is used as an inductor must be thin enough to flow current by a tunnel mechanism.

- (III) There is a case in which an organic coloring matter is an inductor but is not as thin as in the case of (II), although the concept is similar to the one of (II). In this case, a mechanism is as follows; when the work function of the conductive material (9) and the work function of the conductive material (12) are different from each other, an electric potential gradient is generated inside the element based on difference in work function of both conductive materials, and pairs of an electron and a hole generated in the organic coloring matter layer and the π -conjugated high polymer layer due to irradiation are efficiently separated so that electromotive force (or current) is taken out to outside. The conversion efficiency is believed to be higher as the difference in work function between both conductive materials is larger. At this time, when resistance of the π -conjugated high polymer layer is significantly lower than the one of the organic coloring matter layer by doping and the like, electric potential difference generated by the difference in work function of both conductive materials is almost applied into the organic coloring matter layer. Therefore, it is considered that pairs of an electron and a hole formed by light generated in the organic coloring matter layer can be separated efficiently.

As described above, various photoelectric conversion mechanisms are given. In any case, the organic coloring matter and the π -conjugated high polymer are combined to be used to broaden a wavelength region of light that can be used to improve photoelectric conversion efficiency remarkably.

As a conductive material that is used in one embodiment of the present invention, a metal that has the higher work function such as gold, platinum, chromium, and palladium, a metal that has the lower work function such as indium, aluminum, gallium, and an alloy of indium and gallium, metal oxide such as tin oxide, indium

oxide, and indium tin oxide (ITO), carbon and the like are given.

In addition, when the π -conjugated high polymer layer is directly formed and deposited by the first conductive material due to polymerization in electric field, the metal that has the higher work function, the metal oxide, carbon and the like are preferably used as a conductive material.

As the second conductive material which is in contact with the organic coloring matter layer, a conductive material which can have an ohmic contact to the organic coloring matter layer is selected in the case of forming a P-n hetero junction of the photoelectric conversion mechanism (I); the metal that has the lower work function is used in the case of n-type organic coloring matter layer; and the metal that has the higher work function is used in the case of P-type organic coloring matter layer. In a photoelectric conversion element using the MIS element structure of the photoelectric conversion mechanisms (II) and (III), a metal is used, which is expected to form a schottky junction with a π -conjugated high polymer, namely, the metal that has the lower work function is used in the case of a P-type π -conjugated high polymer; the metal that has the higher work function is used in the case of an n-type π -conjugated high polymer. Of course, two or more conductive materials as described above may be stacked to be used in each case.

As for a structure of an electrode which is formed of a light-transmitting conductive material used in one embodiment of the present invention, there is no particular problem when a transparent electrode is used. However, metal is usually deposited on the organic coloring matter layer or the π -conjugated high polymer by vacuum deposition, sputtering, CVD (chemical vapor deposition), coating and the like in order to form a semi-transparent electrode.

The light-transmission efficiency of the conductive material at this time is determined by considering contact resistance of the conductive material and the organic coloring matter layer or the π -conjugated high polymer layer, and resistance of the conductive material itself. Usually, the efficiency is controlled between 5 and 90 %. On the other hand, in the P-n type photoelectric conversion element, a comb-shaped electrode structure is preferred to be used as an electrode structure on the side that is

irradiated with light in order to take incident light effectively.

It is to be noted that glass, ceramic and plastic are given as a substrate when the conductive material is provided over the substrate in the photoelectric conversion element according to one embodiment of the present invention.

As a π -conjugated high polymer used in one embodiment of the present invention, the one having a conjugated double bond in a framework of a chemical structure such as polyacetylene, polypyrrole, polythienylene, polyaniline, polyphenylenes, polyphenylene sulfide and polyphenylene oxide is used.

In addition, it is preferred to perform doping for the purpose of reducing internal resistance of the π -conjugated high polymer. Usually, a π -conjugated high polymer is an insulating material itself. The π -conjugated high polymer can be a P-type or an n-type material by doping an electron acceptor (e.g. bromine, iodine, bromine iodide, arsenic pentafluoride, perchlorate oxygen and the like) or an electron donor (e.g. Na, K, Li, amine and the like), and the conductivity thereof is universally and broadly controlled from a semiconductor region to a metal region.

Among π -conjugated high polymers, the one that can be formed by electrolytic polymerization is preferably used since it has advantages that doping is performed at the same time when it is formed and the thickness of a generated high polymer film can be controlled by the amount of conduction charges. As such a π -conjugated high polymer that can be formed by electrolytic polymerization, a homopolymer of pyrrole, a homopolymer of N-substituted pyrrole, a copolymer of pyrrole and N-substituted pyrrole, polythienylene (polythiophene), polyaniline, polyfuran, polyazulene and the like are given, each of which can be easily formed by electrolytic polymerization. When these π -conjugated high polymers are used for a photoelectric conversion element in one embodiment of the present invention, one of the π -conjugated high polymers may be used alone, or alternatively, two or more such π -conjugated high polymer materials may be stacked to be used depending on the light absorption property of the material.

As an organic coloring matter used in one embodiment of the present invention, the one having the absorption capability of light of a particular wavelength can be used. Considering the photoelectric conversion efficiency, an organic coloring matter is

preferable, which is capable of suppressing recombination of holes in the coloring matter and moving the holes to the π -conjugated high polymer side effectively in order to sensitize a π -conjugated high polymer layer. As such a coloring matter compound, for example, a xanthene based compound such as rhodamine B, a phenazine based compound such as safranin T, a phenothiazine based compound such as thionine and methylene blue, a cyanine based compound such as merocyanine and phthalocyanine can be given. As shown in FIG. 2, these organic coloring matters are formed in layer on the π -conjugated high polymer layer. A method of forming them may be a usual solvent casting method (including spinner coating or spray coating) or deposition. A thick film is preferably in a range of 200 Å to 1 μ m considering that there are no pinholes and internal impedance of the coloring matter is prevented from increasing excessively. Pinholes are easily generated below 200 Å whereas the internal impedance of the coloring matter increases too much over 1 μ m.

Also in this case, two or more organic coloring matters are stacked to be used in accordance with the light absorption property of the organic coloring matter. In addition, when the organic coloring matter is deposited on the π -conjugated high polymer layer to which doping is performed, the organic coloring matter also serves as a protective film for the π -conjugated high polymer layer, thereby resulting in more stable operation.

It is to be noted that irradiation is conducted from the upper side in the FIG. 2; however, irradiation may be also conducted from the lower side with no problems when the conductive material (9) can transmit light. Moreover, one side or all sides of the photoelectric conversion element according to one embodiment of the present invention may be sealed with a material which does not disturb light transmission or, for example, blocks only ultraviolet rays such as a silicon resin and an epoxy resin.

The present invention will be described in detail hereinafter by embodiments, but the invention is not limited thereto.

[Embodiment 1]

A chromium (Cr) layer of 1000 Å thick is provided over a glass substrate of 3.5 cm \times 7 cm by vacuum deposition and a gold (Au) layer of 2000 Å thick is further

provided thereon by vacuum deposition to form a working electrode (i) (an effective working electrode area is $2\text{ cm} \times 3.5\text{ cm}$). Pyrrole (0.07 g), N-methylpyrrole (0.35 g) and tetraethylene ammonium perchlorate (0.7 g) are solved in acetonitrile of 100 ml to provide a reaction solution (i). A platinum (pt) electrode is used as a counter electrode and SCE (saturated calomel electrode) is used as a reference electrode, and they are soaked in the reaction contact solution (i) with the working electrode (i). Then, a certain amount of current (0.15 mA) is applied using the working electrode as an anode between the working electrode and the counter electrode for 90 minutes under a nitrogen gas atmosphere to form a π -conjugated high polymer layer of approximately 4000 \AA on the working electrode (i). Thereafter, vacuum drying is performed after washing using acetonitrile so that a π -conjugated high polymer sample (i) is obtained. Next, a merocyanine coloring matter (by Japan photosensitive pigment Research Institute: NK-2045) is further provided on the π -conjugated high polymer layer sample (i) with a thickness of 800 \AA by vacuum deposition, and further, an aluminum (Al) layer is vacuum-deposited thereon. At this time, the light-transmission efficiency of the Al layer alone is 10 % to simple-color light of 500 nm. The photoelectric conversion element sample that is obtained as described is to be a sample (i).

[Embodiment 2]

As in Embodiment 1, by using the π -conjugated high polymer layer sample (ii) that is obtained in Embodiment 1, rhodamine B that is an organic coloring matter is vacuum-deposited to a thickness of 1000 \AA . Further, the Al layer is vacuum-deposited thereon under the same condition as in Embodiment 1. The photoelectric conversion element sample that is obtained as described is to be a sample (ii).

[Embodiment 3]

The working electrode (i) obtained in Embodiment 1, and the counter electrode and the reference electrode that are used in Embodiment 1 are used to form a polythiophene film of approximately $1\text{ }\mu\text{m}$ according to a method by Kondo et al. (publication: J, O, B, Chem. Commun.) p. 882, 1988 so that a π -conjugated high polymer layer sample (ii) is obtained. Next, on the π -conjugated high polymer layer sample (ii), a merocyanine coloring matter and an Al layer are vacuum-deposited as in

Embodiment 1 to obtain a photoelectric conversion element sample. This sample is to be a sample (iii).

[Comparative example 1]

On the π -conjugated high polymer layer sample (i) that is obtained in Embodiment 1, an Al layer is vacuum-deposited as in Embodiment 1. This is to be a comparative sample (i).

[Comparative example 2]

On the working electrode (i) that is obtained in Embodiment 1, a merocyanine coloring matter and an Al layer are vacuum-deposited as in Embodiment 1. This is to be a comparative sample (ii).

[Comparative example 3]

On the working electrode (i) that is obtained in Embodiment 1, rhodamine B and an Al layer are vacuum-deposited as in Embodiment 2. This is to be a comparative sample (iii).

The photoelectric conversion property of the samples (i) to (iii) and the comparative samples (i) to (iii) that are obtained in the Embodiments 1 to 3 and the comparative examples 1 to 3 is made to be positive on Au side of each sample and negative on Al side. Then, each test that will be described hereinafter is conducted.

[Photoelectromotive Force Test]

Each sample is irradiated with light that is 10 mW/cm^2 on the exposed surface from the Al electrode side of each sample by using a xenon lamp of 250 W, a UV cut filter (UV-38 by Toshiba) and an IR cut filter (HA-30 by Hoya glass). The open circuit voltage V_{oc} (mV) generated in each sample after 3 minutes of the start of irradiation and short-circuit current I_{sc} ($\mu\text{A/cm}^2$) are collectively shown in Chart 1.

Chart 1: Voc and Isc of each sample

	Sample (i)	Sample (ii)	Sample (ii)	Comparative Sample (i)	Comparative Sample (ii)	Comparative Sample (iii)
Voc (mv)	560	420	550	—	580	380
Isc ($\mu\text{A}/\text{cm}^2$)	14	1.8	4.6	—	3.1	0.05

(— : Not Observed)

According to the above chart, the photoelectric conversion element of the present invention is characterized in that the photoelectromotive force is excellent and the current density is particularly large.

[Wavelength Dependency Test]

The sample (i) and the comparative sample (ii) are irradiated with light that is 1 mW/cm² on the exposed surface from the Al electrode side by using a xenon lamp of 250 W and a band pass filter Toshiba interference filter: KL-42~KL 65) in order to measure Voc (mv) light wavelength (nm dependency. Results of the measurement are shown in FIG. 3.

Reference numeral (A) denotes characteristics of the sample (i), and (B) denotes characteristics of the comparative sample (ii) in the figure.

According to FIG. 3, it is understood that the photoelectric conversion element of the present invention characteristically responds to light of the long wavelength side.

In addition, according to the results of the photoelectromotive force test and the wavelength dependency test, it is also understood that the photoelectric conversion element of the present invention has excellent conversion efficiency to visible light.

[Stability and Responsiveness Test]

Under irradiation of the photoelectromotive force test, change in Voc (mv) of the sample (i) by ON/OFF repetition of irradiation at the ratio of 1 minute for 1 cycle is observed. The recorder trace of the results of measurement is shown in FIG. 4.

Reference numerals (C), (D), (E) and (F) in the figure each show the value of Voc (mv) of the first, the second, the 200th and the 201st ON/OFF.

According to FIG. 4, it is understood that the photoelectric conversion element of the present invention has excellent stability and excellent responsiveness.

[Lifetime Test]

The sample (i) is sealed with a silicon resin (by Shinetsu Silicon: KE-106) and irradiated with light for 300 hours continuously under the condition of irradiation of the photoelectromotive force test. Then, change of Voc and Isc over time is measured. As a result, it is shown that retention of both Voc and Isc is 90 % or more of the initial state.

Therefore, it can be said that the photoelectric conversion element according to the present invention has a longer lifetime as an organic element.

As described above, the present invention can provide a low-priced and long-lived photoelectric conversion element in which a response wavelength region is broadened and photoelectric conversion efficiency is high by providing a first and a second conductive materials at least one of which can transmit light and a π -conjugated high polymer layer and an organic coloring matter layer which are interposed between the first and the second conductive materials. The photoelectric conversion element can be broadly applied, e.g. to a solar battery, a color sensor, a color recognizing sensor and the like.

4. Brief Description of the Drawings

FIG. 1 is a cross-sectional view of a conventional photoelectric conversion element; FIG. 2 is a cross-sectional view of a photoelectric conversion element in one embodiment of the present invention; FIG. 3 is a figure showing change in open circuit voltage Voc (mv) by wavelength of irradiation light (nm) of a photoelectric conversion element that is a comparative example of the photoelectric conversion element in one embodiment of the present invention; FIG. 4 is a figure showing change in open circuit voltage Voc (mv) by ON/OFF repetition rate of the irradiation of the photoelectric conversion element in one embodiment of the present invention.

In the drawings, reference numeral (1) denotes a transparent or a semi-transparent electrode; (2) denotes an organic compound layer; (3) denotes an electrode; (4) and (6) denote lead jointing terminals; (5) and (7) denote lead wires; (8)

denotes irradiation light; (9) and (12) denote conductive materials; (10) denotes a π -conjugated high polymer layer; (11) denotes an organic coloring matter layer; (13) and (16) denote lead jointing terminals; (14) and (16) denote lead wires; (A) denotes photoelectric characteristics of the sample (i); (B) denotes photoelectric characteristics of the comparative sample (ii); (C), (D), (E) and (F) each denote photoelectric characteristics of the first, the second, the 200th and the 201st ON/OFF repetition of irradiation.

It is to be noted that the same reference numerals denote the same or corresponding portions in the drawings.

Agent: Masuo Oiwa

Amendment of Proceedings (Voluntary)

November 26, 1983

To Commissioner, Patent Office

1. Case Identification Patent Application No.: Sho58-188224

2. Title of the Invention

Photoelectric Conversion Element

3. Amender:

Relation to the Case: Applicant

Address: 2-2-3, Marunouchi, Chiyoda-ku, Tokyo

Name: (601) Mitsubishi Electric Corporation

Representative: Nihachiro Katayama

4. Agent

Address: 2-2-3, Marunouchi, Chiyoda-ku, Tokyo

c/o Mitsubishi Electric Corporation

Name: (7375) Patent Attorney, Masuo Oiwa

(Contact Information: 03-213-3421, Patent Division)

5. Items Amended

Scope of Claims, the Detailed Description of the Invention and the Brief Description of the Drawings in the Specification

6. Contents of Amendment

(1) Scope of claims in the specification is amended as attached.

(2) "gold platinum" in the line 20 on the page 7 in the specification is amended to "gold, platinum".

(3) "is controlled universally" in the line 20 on the page 10 in the specification is amended to "can be controlled".

(4) "reaction contact solution" in the line 4 on the page 14 in the specification is amended to "reaction solution".

(5) "500 mm" in the line 15 on the page 14 in the specification is amended to "500 nm".

(6) "filter Toshiba interference filter" in the line 8 on the page 17 in the specification is amended to "filter (Toshiba interference filter)".

(7) "light wavelength (mm" in the line 5 on the page 17 in the specification is amended to "light wavelength (nm)".

(8) "(mm)" in the line 18 on the page 19 in the specification is amended to "(nm)".

7. List of Attached Document

One document, on which scope of claims after Amendment is described

Scope of Claims

(1) A photoelectric conversion element characterized by having a first conductive material and a second conductive material, at least one of which can transmit light, and a π -conjugated high polymer layer and an organic coloring matter layer which are interposed between the first conductive material and the second conductive material.

(2) The photoelectric conversion element as described in claim 1, in which the π -conjugated high polymer layer is formed using at least one of polyacetylene, polyphenylene, polyphenylene sulfide, polyphenylene oxide, a copolymer of pyrrole and N-substituted pyrrole, a homopolymer of pyrrole, a homopolymer of N-substituted pyrrole, polythienylene, polyaniline, polyfuran and polyazulene.

(3) The photoelectric conversion element as described in claim 1 or 2, in which the organic coloring matter layer is formed using a compound that has a capability to sensitize the π -conjugated high polymer layer.

⑫ 公開特許公報 (A)

昭60—28278

⑤ Int. Cl.⁴
H 01 L 31/10

識別記号

庁内整理番号
6666—5F

④ 公開 昭和60年(1985)2月13日

発明の数 1
審査請求 未請求

(全 8 頁)

⑭ 光電変換素子

① 特 願 昭58—138224

② 出 願 昭58(1983)7月26日

⑦ 発 明 者 角田誠

尼崎市塚口本町8丁目1番1号

三菱電機株式会社材料研究所内

⑧ 発 明 者 肥塚裕至

尼崎市塚口本町8丁目1番1号

⑥ 発 明 者 江藤昌平

尼崎市塚口本町8丁目1番1号

三菱電機株式会社材料研究所内

⑨ 出 願 人 三菱電機株式会社

東京都千代田区丸の内2丁目2

番3号

⑩ 代 理 人 弁理士 大岩増雄 外2名

明 細 書

1. 発明の名称

光電変換素子

2. 特許請求の範囲

(1) 少なくとも一方が透光性である才1、才2導電材料、並びにこの才1、才2導電材料の間に介在された π -共役系高分子層及び有機色素層を備えた光電変換素子。

(2) π -共役系高分子層が、ポリアセチレン、ポリフェニレン類、ポリフェニレンスルフィド、ポリフェニレンオキシドピロールとN-置換ピロールの共重合体、ピロールのホモポリマー、N-置換ピロールのホモポリマー、ポリチエニレン、ポリアニリン、ポリフランおよびポリアズレンの内の少くとも一種で形成される特許請求の範囲才1項記載の光電変換素子。

(3) 有機色素層が π -共役系高分子層を増感する能力を有する化合物で形成されている特許請求の範囲才1項または才2項記載の光電変換素子。

換素子。

3. 発明の詳細な説明

この発明は新規な光電変換素子に関する。

従来、光電変換素子としては、主としてシリコン半導体の表面近くにP- π 接合をつくることにより得られるいわゆる太陽電池が考案され実用化されている。しかし、これとは別にもつと安価な有機材料、たとえばポリアセチレンなどの導電性高分子材料を半導体として利用したものや、たとえばフタロシアニンなどの有機色素の光増感能を利用したものなどの検討も行われている。

これら有機材料を用いたサンドイッチタイプの光電変換素子は主として才1図に示したような構造のものである。

この動作原理は、透明または半透明電極(1)を通過した光(8)が、有機化合物層(2)に入射すると、透明または半透明電極(1)と有機化合物層(2)の界面に電位差が生じ、リード線(6)および(7)の間に光誘起電力が発生するというものである。この

場合、透明または半透明電極(11)と有機化合物層(12)との間には異方接合(例えばP-n接合)やショットキー接合などができていることが必要で、さらに有機化合物層と電極(13)は等方接合、例えばオーミック接触になつていなければならない。さらに詳しく言うと、光照射下でのそれ自身の仕事関数(フェルミ単位)の値が透明または半透明電極>有機化合物層≈電極、または透明または半透明電極<有機化合物層≈電極となつていなければならない。リード線(16)、(17)間の電力は、通常前者の場合には(16)が正極、後者の場合には(17)が正極となる。有機光電変換素子とは、このような動作原理を応用しようとするものである。

しかしながらこのような有機材料を用いた光電変換素子は、いずれも光電変換効率が低く、得られる光起電力が不安定で、寿命が短いというような欠点があり、実用化のためには解決すべき問題点が多数残されている。

この発明は上記従来のものの欠点を除去する

ためになされたもので、少なくとも一方が透光性である才1、才2導電材料並びにこの才1、才2導電材料の間に介在された π -共役系高分子層及び有機色素層を備えることにより、応答波長域が拡大し、光電変換効率が高く、安価で、長寿命の光電変換素子を提供することを目的とする。

才2図は、この発明の一実施例の光電変換素子の断面図である。即ち、(9)および(10)は導電材料で、基板上に導電材料層を設けることによつても得られるが図は簡単のため導電材料単独で用いた場合を示す。又、少なくとも光照射側の導電材料(10)は透光性である。導電材料(9)上に π -共役系高分子層(11)を設け、その上に有機色素層(12)を設け、さらに導電材料(10)を被着してなるものであり、導電材料(9)および(10)にリード線(16)および(17)を結着し、電力を取り出せるようにしたものである。なお(17)、(18)はリード接続端である。

この発明の一実施例の光電変換素子は上記の

ように構成されており、この光電変換素子の動作原理の詳細は現時点では不明であるが、この発明者等は以下に述べるような光電変換機構のいずれか、又は二つ以上の混り合つた機構を考えている。即ち、

(I) π -共役系高分子がP型の材料であり、有機色素がn型である場合には π -共役系高分子と有機色素との間でP-n型のヘテロ接合が形成され、光照射下では接合領域で発生したキャリアー(電子および正孔)が接合領域内での電界によつて電荷分離を起こし外部に起電力(または電流)を誘起させる機構が考えられる。ここで π -共役系高分子がn型、有機色素がP型である場合でも同様の結果が得られるものと考えられる。

(II) π -共役系高分子がP型またはn型の物質であれば、P型の π -共役系高分子と仕事関数の小さい金属との間でショットキー型の接合が形成できると思われる。n型の π -共役系高分子であれば仕事関数の大きい金属との間でショ

ットキー型の接合が形成できると期待される。ショットキー型の接合素子はそれ自身で光電変換素子として利用できるが光電変換能を高めるためにMIS型素子(M:金属, I:誘電体, S:半導体)が考えられており、この素子では単なるショットキー型の素子に比べ開放端電圧が上昇することが知られている。

このMIS型素子における誘電体として有機色素を用いるという考え方である。

ここで有機色素は単なる誘電体ではなく半導体部で利用できない波長の光を吸収してキャリアーを発生させ、そのキャリアーを半導体および金属に電荷を注入し変換効率を高めようとする考え方である。この場合、誘電体として用いる有機色素の厚膜(層膜)はトンネル機構で電流が流れる程度に薄くなければならない。

(III) (II)の考え方と良く似ているが、有機色素が誘電体でありかつ(II)の場合程薄膜でない場合がある。この場合、導電材料(9)の仕事関数と導電材料(10)の仕事関数が異なる時両導電材料の仕事

関数差に基づき素子内部に電位勾配が生じ有機色素層および π -共役系高分子層中で光照射によつて発生した電子-正孔対を効率よく分離することによつて外部に起電力(または電流)を取り出す機構である。この時両導電材料間の仕事関数差が大きい程変換効率は大きくなると考えられる。この時、 π -共役系高分子層がドーピング処理等の方法でその抵抗が有機色素層のそれに比べて著しく低ければ、両導電材料の仕事関数差により発生する電位差は有機色素層に殆んど印加され、有機色素層内で発生する光による電子-正孔対をより効率よく分離することができると考えられる。

以上のように光電変換機構としては種々考えられるが、いずれの場合も有機色素と π -共役系高分子を組み合わせて用いることによつて利用可能な光の波長領域を広げ光電変換効率を著しく上げようとするものである。

この発明の一実施例に用いる導電材料としては、金白金、クロムおよびパラジウムなどの仕

事関数の大きい金属、インジウム、アルミニウム、ガリウムおよびインジウムとガリウムの合金などの仕事関数の小さい金属、錫酸化物、酸化インジウム、およびインジウム・錫酸化物(ITO)などの金属酸化物、並びにカーボンなどがあげられる。

又、才1導電材料が π -共役系高分子層を電界重合により直接合成・被着させる場合には、導電材料としては、上記仕事関数の大きい金属、上記金属酸化物およびカーボンなどが好んで用いられる。

さらに有機色素層と接する才2導電材料としては、前記光電変換機構(1)のP-n型のヘテロ接合が形成される場合は有機色素層とオーミック接触をとり得る導電材料が選ばれ、有機色素層がn型の時には上記仕事関数の小さい金属が用いられ、有機色素層がP型の時には上記仕事関数の大きい金属が用いられる。光電変換機構(4)、(5)のMIB型の素子構造を利用した光電変換素子では π -共役系高分子とショットキー型

接合を形成すると期待される金属、すなわち、 π -共役系高分子がP型である場合には上記仕事関数の小さい金属が、n型の π -共役系高分子を用いる時には上記仕事関数の大きい金属が用いられる。勿論、各場合において、上記導電材料を2つ以上重ねて用いても良い。

この発明の一実施例に用いる透光性の導電材料で形成される電極構造としては透明電極を用いる時は特に問題はないが、通常、半透明になるように金属を有機色素層または π -共役系高分子上に真空蒸着、スパッタリング、CVD(ケミカル・ベーパー・デポジション)およびメッキ等の方法によつて被着させる。

この時の導電材料の光透光率としては導電材料と有機色素層または π -共役系高分子層との接触抵抗や導電材料自身の抵抗を考慮して決められ通常5から90%の間に制御される。一方、P-n型の光電変換素子においては光照射側の電極構造としては入射光を有効にとり入れるべく、くし型の電極構造が好んで用いられる。

なお、この発明の一実施例の光電変換素子において導電材料が基板上に設けられている場合、基板としては、ガラス、セラミック、およびプラスチックなどがあげられる。

この発明の一実施例に用いる π -共役系高分子としては、例えばポリアセチレン、ポリピロール、ポリチエニレン、ポリアニリン、ポリフエニレン類、ポリフエニレンスルフィド、ポリフエニレンオキシドなど化学構造の骨格に共役二重結合を有するものが用いられる。

又、 π -共役系高分子の内部抵抗を下げる目的でドーピング処理を行なうことが好ましい。通常、 π -共役系高分子はそれ自身では絶縁体であるが電子受容体(例えば臭素、ヨウ素、ヨウ化臭素、五フッ化ヒ素、および過塩素酸素等)および電子供与体(例えばNa, K, Li, およびアミン等)をドーピングすることによつて、それぞれP型およびn型の材料にすることができ、その電導度も半導体領域から金属領域まで幅広く制御可能である。

π -共役系高分子の中でも電解重合によつて合成可能なものは合成時にドーピング処理が同時に行なわれること、生じた高分子膜の厚みを通電電荷量によつて制御できる等の利点を有していることから好んで用いられる。このような電解重合法で合成できる π -共役系高分子としてはピロールのホモポリマー、N-置換ピロールのホモポリマー、ピロールとN-置換ピロールの共重合体、ポリチエニレン(ポリチオフェン)、ポリアニリン、ポリフランおよびポリアズレン等があげられ、いずれも電解重合によつて容易に合成できる。これら π -共役系高分子をこの発明の一実施例の光電変換素子に用いる場合は単独もしくは上記高分子材料を材料の光吸収特性に応じて二種以上重ねて用いても良い。

この発明の一実施例に用いる有機色素としては、特定の波長の光を吸収する能力を有するものであれば使用可能であるが、光電変換効率を考慮すると、色素内でのホールの再結合を抑えて、 π -共役系高分子側に効率良く移動させる

有機色素を被着させることは π -共役系高分子層の保護膜ともなり動作安定性を一段と増す結果につながっている。

なお、前記図2図では、上方から照射を行なっているが、導電材料(9)を透光性とすれば下方から光照射を行なつても差しつかえない。また、この発明の一実施例の光電変換素子の片面あるいは全面を光透過性を損わない材料もしくは例えば紫外線のみ遮断する材料など、例えばシリコン樹脂、エポキシ樹脂などで封止してもよい。

以下実施例によりこの発明を詳細に説明するが、これによりこの発明を限定しない。

実施例 1

8.5 cm × 7 cm のガラス基板上に真空蒸着法によつて厚さ1000 Å のクロム(Cr)膜を設け、更にこの上に金(Au)膜を2000 Å の厚さに真空蒸着法によつて設けたものを作用電極(1)とした(有効作用電極面積は2 cm × 3.5 cm)。100 mg のアセトニトリルにピロール(0.07 g)、N-メチルピロール(0.85 g)およびテトラエチ

ルアンモニウムパークロレート(0.7 g)を溶解させた液を反応溶液(1)とした。対極として白金(Pt)電極を、参照電極として80 B(飽和カロメル電極)を使用し、反応溶液(1)中に、作用電極(1)と共に浸し、窒素ガス雰囲気下で、作用電極を陽極として対極との間に一定電流(0.15 mA)を90分間流し、作用電極(1)上に π -共役系高分子層を約4000 Å の厚さに形成し、アセトニトリルで洗浄後真空乾燥を行い、 π -共役系高分子試料(1)を得た。次に π -共役系高分子層試料(1)上にさらに真空蒸着法でメロシアン色素(日本感光色素社製:NE-2045)を800 Å の厚さで設け、さらにその上にアルミニウム(Al)層を真空蒸着した。このときのAl層単独の光透過率は500 nmの単色光に対して10%であつた。このようにして得た光電変換素子試料を試料(1)とする。

この場合においても有機色素の光吸収特性に応じて二種以上を重ねて用いてもよい。また、ドーピング処理された π -共役系高分子層上に有機

ルアンモニウムパークロレート(0.7 g)を溶解させた液を反応溶液(1)とした。対極として白金(Pt)電極を、参照電極として80 B(飽和カロメル電極)を使用し、反応溶液(1)中に、作用電極(1)と共に浸し、窒素ガス雰囲気下で、作用電極を陽極として対極との間に一定電流(0.15 mA)を90分間流し、作用電極(1)上に π -共役系高分子層を約4000 Å の厚さに形成し、アセトニトリルで洗浄後真空乾燥を行い、 π -共役系高分子試料(1)を得た。次に π -共役系高分子層試料(1)上にさらに真空蒸着法でメロシアン色素(日本感光色素社製:NE-2045)を800 Å の厚さで設け、さらにその上にアルミニウム(Al)層を真空蒸着した。このときのAl層単独の光透過率は500 nmの単色光に対して10%であつた。このようにして得た光電変換素子試料を試料(1)とする。

実施例 2

実施例1で得た π -共役系高分子層試料(1)を用いて、この上に実施例1と同様に、有機色素

のローダミンBを1000Åの厚さに真空蒸着し、さらにその上に実施例1と同様の条件でA2層を真空蒸着した。このようにして得た光電変換素子試料を試料Hとする。

実施例8.

実施例1で得た作用電極(H)、および実施例1で用いた対極および参照電極を用い、金藤らの方法(出版物 J. O. S. Chem. Commun.) P. 882, 1988年に従つて約1μm厚のポリチオフェン膜を合成し、π-共役系高分子層試料Hを得た。次にπ-共役系高分子層試料H上に、実施例1と同様にメロシアニン色素およびA2層を真空蒸着し、光電変換素子試料を得た。これを試料Hとする。

比較例1.

実施例1で得たπ-共役系高分子層試料(H)上に実施例1と同様にA2層を真空蒸着した。これを比較試料(H)とする。

比較例2.

実施例1で得た作用電極(H)上に、実施例1と

同様にメロシアニン色素およびA2層を真空蒸着した。これを比較試料Hとする。

比較例3

実施例1で得た作用電極(H)上に、実施例2と同様にローダミンBおよびA2層を真空蒸着した。これを比較試料Hとする。

上記実施例(II~III)および比較例(III~III)で得た試料(H)~(H)および比較試料(H)~(H)について光電変換特性を、各試料のAu側を正、A2側を負として以下に示す各試験により行なつた。

光起電力試験

250Wのクセノンランプおよび紫外線カットフィルター(東芝製UV-88)、熱線カットフィルター(保谷ガラス製HA-80)を用いて受光面で10mW/cm²の光を各試料のA2電極側から照射した。光照射開始8分後に各試料が発生した開放端電圧Voc(mV)および短絡電流Isc(μA/cm²)を表1にまとめて示す。

表1. 各試料のVocおよびIsc

	試料(H)	試料(H)	試料(H)	比較試料(H)	比較試料(H)	比較試料(H)
Voc(mV)	580	420	550	—	580	380
Isc(μA/cm ²)	1.4	1.8	4.6	—	8.1	0.05

(— : 観測されなかつた)

上表から、この発明の光電変換素子は優れた光起電力を示し、特に大きな電流密度の得られるのが特徴であるといえる。

波長依存性試験

250Wのクセノンランプおよびバンドパスフィルター東芝干渉フィルター: KL-42~KL65)を用いて、受光面で1mW/cm²の光を試料(H)および比較試料(H)のA2電極側から照射し、Voc(mV)光波長(nm)依存性を測定した。測定結果を才8図に示す。

図中(H)は試料(H)、(H)は比較試料(H)の特性である。

才8図から、本発明の光電変換素子は特徴的

に長波長側の光に対しても応答することがわかる。

また、光起電力試験および波長依存性試験の結果から、この発明の光電変換素子は可視光に対して優れた変換効率を示すものであることがわかる。

安定・応答性試験

光起電力試験の光照射下で、試料(H)について1周期1分の割合で光照射のON/OFFの繰り返しによるVoc(mV)の変化を測定した。測定結果のレコーダー・トレースを才4図に示す。

図中(H)(H)はそれぞれ1回目、2回目、200回目、201回目のVoc(mV)の値を示す。

才4図から、この発明の光電変換素子は、優れた安定性および優れた応答性を示すことがわかる。

寿命試験

試料(H)をシリコン樹脂(信越シリコン社製: KM-106)で封止し、光起電力試験の光照射条件下で連続800時間光照射を行い、Voc

および I_{sc} の経時変化を測定した。その結果、 V_{oc} および I_{sc} 共初期の 90% 以上の保持率を示した。

このことから、この発明の光電変換素子は有機系素子としては長寿命のものであるといえる。

以上説明したとおり、この発明は、少なくとも一方が透光性である才1、才2導電材料並びにこの才1、才2導電材料の間に介在されたπ-共役系高分子層及び有機色素層を備えることにより、応答波長域が拡大し、光電変換効率が高く、安価で、長寿命の光電変換素子を得ることができ、例えば太陽電池、カラーセンサー、および色彩認識センサーなどに広く適用できる。

4. 図面の簡単な説明

才1図は従来の光電変換素子の断面図、才2図はこの発明の一実施例の光電変換素子の断面図、才3図はこの発明の一実施例の光電変換素子との比較例のその照射光波長 (nm) による開放端電圧 V_{oc} (mV) 変化を示す特性図、才4図はこの発明の一実施例の光電変換素子の、

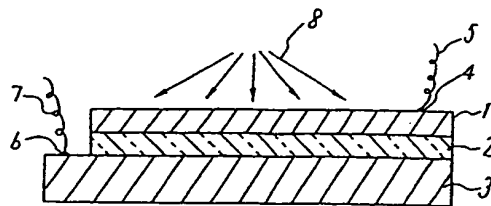
光照射の ON/OFF 繰返し回数による開放端電圧 V_{oc} (mV) 変化を示す特性図である。

図において、(1)は透明または半透明電極、(2)は有機化合物層、(3)は電極、(4)、(6)はリード接続端、(5)、(7)はリード線、(8)は照射光、(9)、(10)は導電性材料、(11)はπ-共役系高分子層、(12)は有機色素層、(13)、(14)はリード接続端、(15)、(16)はリード線、(17)は試料(1)の光電特性、(18)は比較試料(2)の光電特性、(19)(20)(21)は各々光照射の ON/OFF 繰返し回数1回目、2回目、200回目、201回目の光電特性を示す。

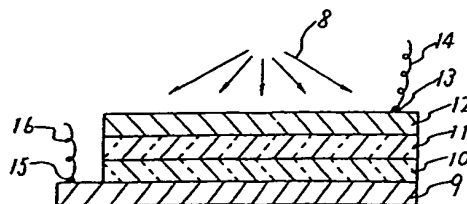
なお図中同一符号は同一又は相当部分を示す。

代理人 大 岩 増 雄

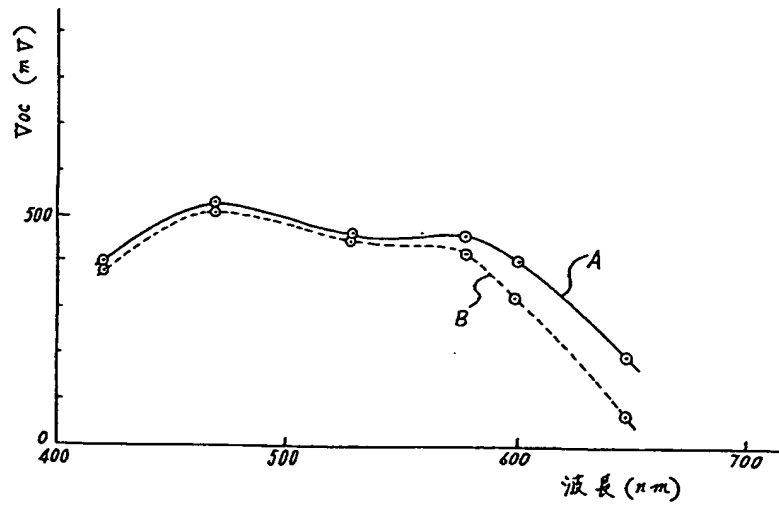
第1図



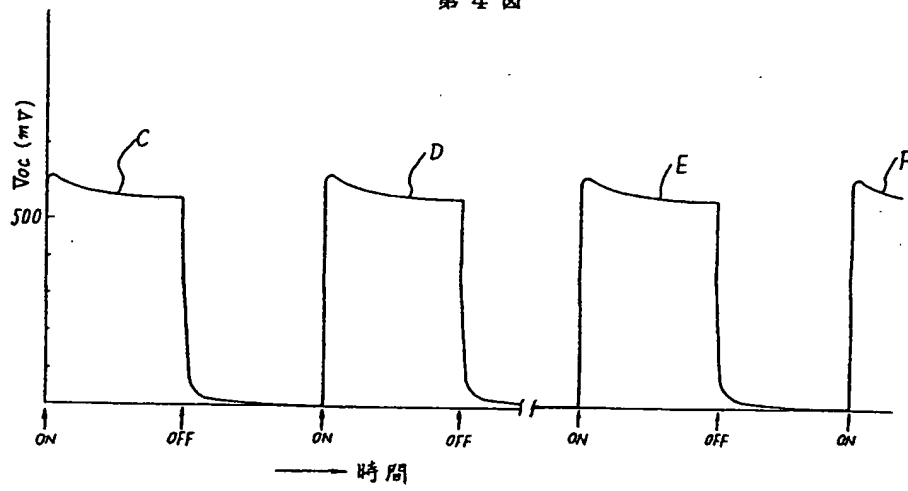
第2図



第3圖



第4圖



手続補正書(自発)

昭和58年11月26日

特許庁長官殿

1. 事件の表示 特願昭58-188224号

2. 発明の名称 光電変換素子

3. 補正をする者

事件との関係 特許出願人
住 所 東京都千代田区丸の内二丁目2番3号
名 称 (601)三菱電機株式会社
代表者 片山 仁 八 郎

4. 代 理 人

住 所 東京都千代田区丸の内二丁目2番3号
三菱電機株式会社内
氏 名 (7375)弁理士 大 岩 増 雄
(連絡先 03(213)3421特許部)



七 式

5. 補正の対象

(明細書の特許請求の範囲および発明の詳細な説明の欄)

6. 補正の内容

- (1) 明細書の特許請求の範囲を別紙のとおり訂正する。
- (2) 同第7頁第20行の「金白金」を「金、白金」に訂正する。
- (3) 同第10頁第20行の「制御万能」を「制御可能」に訂正する。
- (4) 同第14頁第4行の「反応接液」を「反応溶液」に訂正する。
- (5) 同第14頁第15行の「500 mm」を「500 nm」に訂正する。
- (6) 同第17頁下から第8行の「フィルター-東芝干渉フィルター」を「フィルター-(東芝干渉フィルター)」に訂正する。
- (7) 同第17頁下から5行の「光波長(mm)」を「光波長(nm)」に訂正する。
- (8) 同第19頁第18行の「(mm)」を「(nm)」に

訂正する。

7. 添付書類の目録

補正後の特許請求の範囲を記載した書面

1 通

以 上

特許請求の範囲

- (1) 少なくとも一方が透光性である第1、第2導電材料、並びにこの第1、第2導電材料の間に介在された π -共役系高分子層及び有機色素層を備えた光電変換素子。
- (2) π -共役系高分子層が、ポリアセチレン、ポリフエニレン類、ポリフエニレンスルフィド、ポリフエニレンオキシド、ピロールとN-置換ピロールの共重合体、ピロールのホモポリマー、N-置換ピロールのホモポリマー、ポリチエニレン、ポリアニリン、ポリフランおよびポリアズレンの内の少なくとも一種で形成される特許請求の範囲第1項記載の光電変換素子。
- (3) 有機色素層が π -共役系高分子層を増感する能力を有する化合物で形成されている特許請求の範囲第1項または第2項記載の光電変換素子。

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)